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Design principles of natural light-harvesting as revealed by single molecule spectroscopy

T.P.J. Krüger [a,*], R. van Grondelle [b]

[a] Department of Physics, University of Pretoria, Private bag X20, Hatfield 0028, South Africa
[b] Department of Physics and Astronomy, VU University Amsterdam, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

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ABSTRACT

Biology offers a boundless source of adaptation, innovation, and inspiration. A wide range of photosynthetic organisms exist that are capable of harvesting solar light in an exceptionally efficient way, using abundant and low-cost materials. These natural light-harvesting complexes consist of proteins that strongly bind a high density of chromophores to capture solar photons and rapidly transfer the excitation energy to the photochemical reaction centre. The amount of harvested light is also delicately tuned to the level of solar radiation to maintain a constant energy throughput at the reaction centre and avoid the accumulation of the products of charge separation. In this Review, recent developments in the understanding of light-harvesting by plants will be discussed, based on results obtained from single molecule spectroscopy studies. Three design principles of the main light-harvesting antenna of plants will be highlighted: (a) fine, photoactive control over the intrinsic protein disorder to efficiently use intrinsically available thermal energy dissipation mechanisms; (b) the design of the protein microenvironment of a low-energy chromophore dimer to control the amount of shade absorption; (c) the design of the exciton manifold to ensure efficient funneling of the harvested light to the terminal emitter cluster.

1. Introduction

Artificial photosynthesis is envisioned by many to be an important component of mankind's long-term energy solution [1]. Bioinspired photosystems appear most promising, but the first constructs over the past few years have clearly pointed to the infancy of this field [2–4]. To make progress, a very detailed understanding of natural photosynthesis is required in order to wisely extract the most important design principles. Here, the primary steps of photosynthesis – light-harvesting and charge separation – are the most crucial to ensure that the energy of an absorbed photon is stored with a sufficiently high probability, which is commonly 90–100% under conditions of low solar radiation! The design principles of charge separation, which takes place in the so-called reaction centre, are now beginning to be understood. The speed and efficiency of charge separation are based on a finely designed structure that minimises free energy losses, enables selected vibrations to drive quantum coherent processes, and allows control over the multiple pathways that can be followed by an excitation in the reaction centre [5]. The process of photosynthetic light-harvesting has proven to be even more complex. Although a few important design principles can be identified for the purpose of designing synthetic systems [6], many mechanistic details are still incomplete, and further experimental and theoretical advances are awaited to deepen our understanding. One such promising technique is known as single molecule spectroscopy (SMS) and will be the main focus of this Review.

Photosynthetic light-harvesting is performed by an array of interacting chromophores that absorb (solar) photons and transfer the resulting electronic excitation energy to the reaction centre. The chromophores are typically held in fixed positions and orientations by proteins; yet, the protein is much more than a scaffold. It also interacts strongly with the chromophores, thereby significantly altering their spectroscopic and light-harvesting properties. The unique properties of the protein, which underlie its interaction with the chromophores, are unmatched in any solar energy technological device: (a) the protein constitutes a highly heterogeneous dielectric environment, which provides every chromophore with a unique transition energy (also referred to as "site energy") and strongly modifies the electronic couplings amongst the chromophores; (b) the protein is a highly dynamic structure, exhibiting motions on timescales ranging from sub-ps to >1 s, a behaviour commonly referred to as disorder. The structural disorder is not only translated into time-dependent fluctuations of the site energies, but also gives rise to phonons –

* Corresponding author.
E-mail address: tjaart.kruger@up.ac.za (T.P.J. Krüger).

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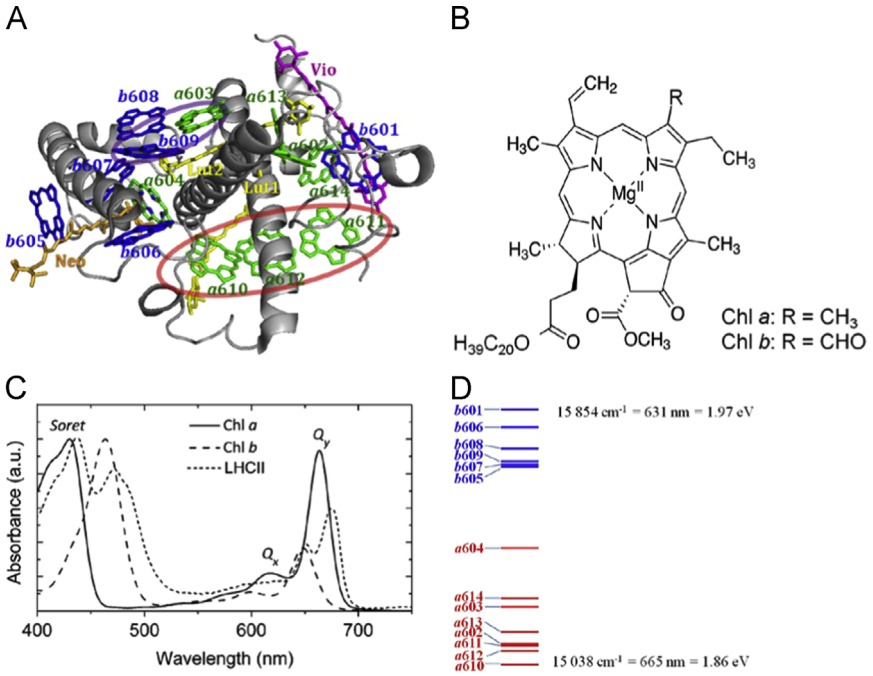

Fig. 1. : (A) Molecular structure of a monomeric subunit of LHCII, based on the X-ray crystallographic data of Ref. [8] at a resolution of 2.72 Å, shown from the outside of the membrane (*i.e.*, stromal view), and using the nomenclature of Ref. [8] for all bound pigments. For clarity, only the chlorin rings of Chl *a* and *b* are shown, in grey and black (online green and blue), respectively. The protein is displayed as four interconnected grey ribbons, and the carotenoids lutein, neoxanthin, and violaxanthin are denoted by Lut, Neo, and Vio, respectively. Encircled are the two Chl clusters that are discussed in the text, *viz.*, 603–609 and 610–611–612. (B) Chemical structure of Chl, differing only at the residue, R, defined bottom right for Chl *a* and *b*. (C) Room-temperature absorption spectrum of Chl *a* (*solid line*) and Chl *b* (*dashed line*) in ethanol, as well as LHC2 (*dotted line*). All three spectra are normalised to the maximum (*i.e.*, at the Soret peak). The three dominant absorption bands, Soret, Q_x and Q_y, are indicated for Chl *a*. (D) Relative values of all Chl site energies in each monomeric subunit of LHC2, according to Ref. [16]. The values of the highest and lowest energies are indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

fast, collective vibrational modes of the protein – which interact with the electronic excited states of the chromophores and consequently change the energy transfer dynamics.

Photosynthetic chromophores are remarkable molecules in several respects. Consider the main light-harvesting complex (LHC) of plants, LHC2, which naturally assembles into a three-fold symmetric structure (*i.e.*, trimer) of identical subunits (*i.e.*, monomers) (Fig. 1A), each containing no less than 14 chlorophylls (Chls) [7,8]. The large conjugated ring of Chl supplies the molecule with a substantial absorption cross section as well as a rigid structure that cannot be easily deformed. Yet, a relatively small modification of the ring can dramatically shift the transition energies: the two types of Chls found in LHC2 – Chl *a* and *b* – differ only at the small side chain *R* (Fig. 1B), but this structural change leads to a 30 nm (*i.e.*, 0.085 eV) shift of the lowest electronic transition (*i.e.*, HOMO to LUMO, also known as Q_y) (Fig. 1C). Likewise, the transition energies of the embedded Chls are tuned by the protein matrix across a large range, providing each Chl in LHC2 with a unique site energy (Fig. 1D). This not only significantly increases the absorption spectral window but also creates an energy gradient, so that the excitation energy can be "funnelled" to a particular site in the LHC or to the reaction centre [9,10]. Another notable property of Chls is their electronic excited states having intrinsic decay times of a few ns. This is six–seven orders of magnitude longer than the timescale of absorption and two–three orders of magnitude longer than the timescale of energy transfer to the reaction centre. In the natural environment, spontaneous emission is therefore a negligible decay channel of the excitation and sufficient time is allowed to initiate the first steps of charge separation. When an LHC is isolated from its natural environment, the fluorescence yield obviously increases considerably and can be used as a probe. Finally, Chls are not only used by plant photosystems as efficient light harvesters but also as energy sinks within an antenna complex or the reaction centre. To this end, a Chl–Chl pair is used to create a charge-transfer state, which can rapidly deplete excitation energy in the antenna or initiate the process of charge separation in the reaction centre [11]. Each monomeric subunit of LHC2 binds four additional chromophores, known as carotenoids (see Fig. 1A). These molecules extend the absorption spectral window by harvesting solar energy in the blue-green spectral region, which is then rapidly transferred to the Chls [12]. Even more important is their photoprotective role whereby Chl singlet and triplet states are efficiently quenched: Chl triplets would otherwise react with oxygen to produce highly reactive (and therefore lethal) singlet oxygen [13]; Chl singlets are quenched when the excitation rate of the photosystem becomes too high (*vide infra*) [14,15].

The chromophores in LHCs occur at an astounding density. For example, the Chl concentration of LHC2 is 0.25 M, which gives Chl–Chl separations as short as 9–10 Å and strong (up to 110 cm^{-1} [16]) interactions amongst the Chls. When the Chls are solubilised at this concentration in an organic solvent with the same average dielectric as the protein, the fluorescence will be virtually zero due to a process known as concentration quenching [17]. Although the arrangement of Chls in LHC2 may appear random, they are actually perfect for optimisation of the energy transfer [6,10,18]. One important reason is that the high chromophore density creates new physical states, known as excitons (the specific type being Frenkel excitons or molecular excitons), whereby the excitation is delocalised over a number of chromophores and hence coherently shared [19]. Excitons significantly decrease the number of pathways that need to be explored during energy migration to the reaction centre, thus leading to shorter transfer times and larger quantum efficiencies. Excitation traps due to single site defects in the antenna network can also be avoided more easily by such a delocalised excitation. The exciton delocalisation length in LHCs is